PHASE-FORMATION PROCESSES IN THE Al₂O₃–ZrO₂–SiO₂ SYSTEM IN HEATING

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The specifics of the phase-formation processes and material structure formation based on Al_2O_3, ZrO_2, and Si_2O_2 are investigated. The possibility of using these materials to protect various construction materials from gas corrosion at high temperatures is demonstrated.

Aluminum and zirconium oxides play a significant role in the production of heat-resistant composite materials [1]. Therefore, studies of phase-formation processes, which determine several of the service and technological properties of composites based on these oxides, are of special interest. For this purpose, we investigated the effect of dispersion of the material, its reactive capacity, and molding pressure on phase-formation processes in materials consisting of mixtures of aluminum, zirconium, and silicon. The raw materials investigated were technical alumina, zirconium dioxide, concentrated quartz sand, and aerosil. All were dried and milled to complete passing via a sieve with a cell size of 480, 10,000, and 13,500 cells/cm². Moreover, siliceous components were represented by polyorganosiloxanes: polyphenilsiloxanes (PPS) and polymethylphenylsiloxanes (PMPS). The compositions of model mixtures are given in Table 1.

The samples were molded as tablets 20 × 20 × 5 mm under a specific pressure of 300, 600, and 900 MPa. Polyorganosiloxanes were introduced in joint dispersing in a ball mill [2].

Heat treatment of samples was carried out in an Emitron electric laboratory furnace with a heating rate of 3.5 – 5.0°C/min and holding 15 min at the maximum temperatures 1100, 1300, and 1600°C.

The phase composition of the samples was studied using x-ray phase analysis on a DRON-2 diffractometer in $Cu_{K\alpha}$ radiation [3].

The diffraction patterns of the initial bicomponent mixtures using aerosil are represented by the reflections of ZrO_2, and in using crystalline SiO_2 by α-quartz reflection as well. Molding at various pressure as well as heat treatment at 1100 and 1300°C does not change the reflection intensity in the diffraction patterns. When heat treated up to 1600°C, SiO_2 in the samples recrystallizes to β-cristobalite, and zircon

($ZrO_2 \cdot SiO_2$) is formed. In this case, the decrease in the size of the particles, the increased content of ZrO_2, and the use of aerosil instead of crystalline silica cause an increase in the zircon reflections. Variation of the molding pressure does not have a substantial effect on the ratio of phases in the fired material. In the case of using crystalline SiO_2 with a particle size below 56 μm, insignificant reflections of α-quartz are observed in the diffraction patterns.

The diffraction patterns of the initial ternary mixtures containing crystalline silica are characterized by the presence of monoclinal ZrO_2, α-quartz, and corundum (Al_2O_3) with insignificant content of χ-Al_2O_3 and θ-Al_2O_3, as well as high-temperature and low-temperature forms of Al_2O_3. α-Quartz reflections are absent on the diffraction patterns of samples containing aerosil.

Firing of samples at temperatures of 1100 and 1300°C results in the residual forms of alumina transforming into corundum. In samples containing aerosil, it is partly transformed into cristobalite at a temperature of 1300°C.

The phase composition of samples after heat treatment at 1600°C depends on the content of the components and their dispersion.

The phase composition of the samples containing 20% amorphous SiO_2 with the initial material particle size not more than 250 μm is represented by α-Al_2O_3, ZrO_2, β-cristobalite, mullite, and zircon. A decrease in the maximum size of the particles to 56 μm produces crystallization of mullite and especially zircon, while the reflections of β-cristobalite are reduced. With a particle size of the initial material not more than 40 μm, β-cristobalite reflections totally disappear.

Zircon reflections are absent in the diffraction patterns containing 20% crystalline SiO whose initial particle size is not more than 250 μm, and β-cristobalite reflections in them are significantly more intense than in the samples containing

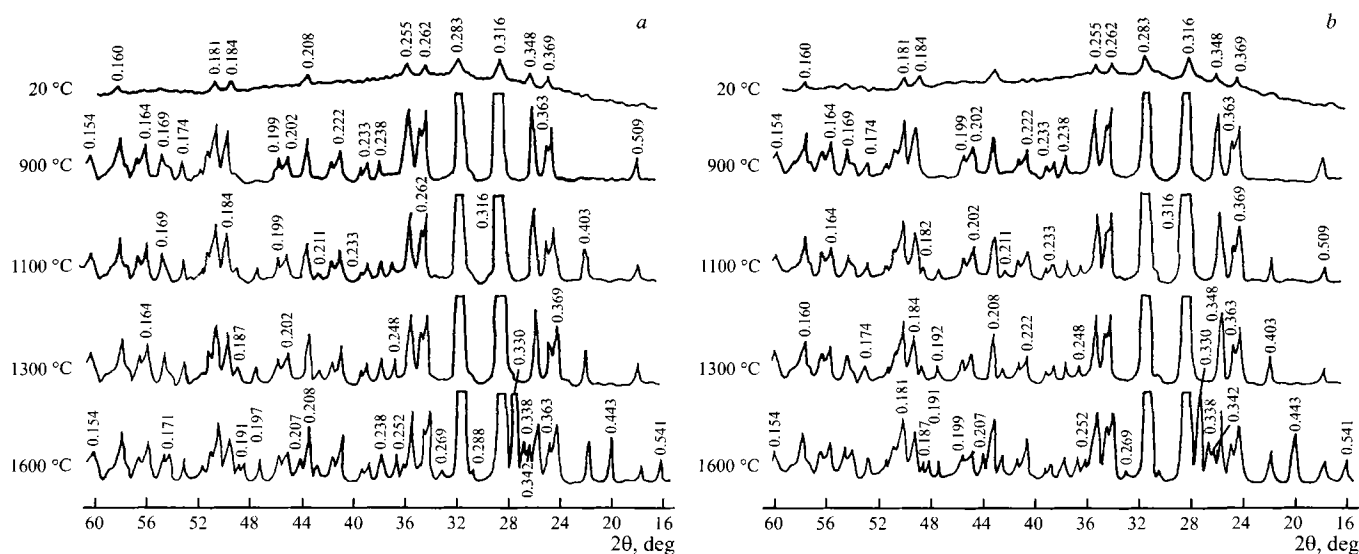[1] National Technical University of Ukraine "KPI", Ukraine.

Fig. 1. Diffraction patterns of ternary systems based on PPS (*a*) and PMPS (*b*) after heat treatment.

cristobalite. An increase in the dispersion of material particles results in the emergence of zircon and mullite reflections, which grow significantly in the samples containing aerosil. Intense formation of mullite and zircon is registered together with a delay in α-quartz conversion to cristobalite.

The introduction of 30% SiO in the mixture composition in both cases decreases the reflections of mullite and increases zircon reflections. The early stage of zircon crystallization can be observed in the samples containing crystalline silica when the particle size is below 250 μm. As the particle size decreases to below 56 μm, α-quartz prevails over β-cristobalite. The diffraction patterns of the samples containing 30% aerosil exhibit the presence of rather perceptible β-cristobalite reflections when the particle size of the initial material is 56 μm.

Patterns of three-component mixtures based on a siloxane binder in their initial state exhibit the maxima of α-Al₂O₃ (d/n = 0.343, 0.255, 0.208, and 0.160 nm) and α-ZrO₂ (d/n = 0.369, 0.316, 0.283, 0.262, 0.254, 0.184, and 0.181 nm). The low intensity of certain reflections and the absence of others are caused by the fact that the oxide grains are densely coated by the x-ray-amorphous polymer (Fig. 1)

Firing at temperature 900°C caused thermal-oxidizing destruction of the organic coating of the polymer. As a result, the existing oxide reflections are sharply intensified, and other α-ZrO₂ reflections (d/n = 0.363, 0.260, 0.222, 0.189, 0.164, 0.154 nm) and α-Al₂O₃ reflections (d/n = 0.403, 0.248, 0.211, 0.192, and 0.187) emerge.

After heating to 1100°C, the intensity of all diffraction reflections increases. The emergence of the weakly intense bands with d/n = 0.403, 0.248, 0.211, 0.192, and 0.187 nm points to the partial crystallization of SiO in the form of β-cristobalite, which is probably caused by disordering of the siloxane chain upon heating.

Further heating up to 1300°C does not produce significant changes in the diffraction pattern. One can only observe a slight increase in the intensity of the β-cristobalite reflections, which is probably accounted for by an increase in the siloxane-chain disordering upon a temperature rise to 1300°C and subsequent chilling.

After firing of samples at 1600°C, the phase composition of the samples is significantly modified: mullite reflections (d/n = 0.541, 0.342, 0.338, 0.288, 0.269, 0.221, and 0.159 nm) and especially intense zircon reflections (d/n = 0.443, 0.330, 0.252, 0.257, 0.191, and 0.191 nm) are registered.

Thus, the use of mechanochemical treatment increased the dispersion of baddeleyite grains and intensified the contact between these grains and polyphenylsiloxane in dispersion, which in heating to 1600°C determined the interaction between ZrO₂ and SiO with the formation of zircon.

It is established that within the temperature range 900 – 1100°C the product of thermal-oxidizing destruction

TABLE 1

Mixture	Weight content, %			
	technical alumina	zirconium dioxide	quartz sand	aerosil
1	–	60	40	–
2	–	60	–	40
3	–	80	20	–
4	–	80	–	20
5	30	40	30	–
6	30	40	–	30
7	40	40	20	–
8	40	40	–	20
9*	35	35	–	30
10**	30	30	–	40

* PMPS.
** PPS.

(siloxane groups) is partially crystallized in the form of β-cristobalite. Heating to 1300°C intensifies crystallization. Interaction between the mixture components proceeds within the temperature range 1300 – 1600°C. The crystal chemical composition of the material is represented by the mullite and zircon phases with additives of non-reacting α-Al_2O_3 and α-ZrO_2 and an insignificant quantity of β-cristobalite.

The size and the shape of crystals in newly formed aluminum silicates to a great extent depend not only on the heating rate but also on the chilling rate. A decrease in the chilling rate increases the size of mullite and sillimanite crystals. Thus, in chilling at a rate of 3000°C/min, the size of the resulting aluminum silicate is on the average 0.3 – 0.5 μm. Chilling at a rate of 250°C/min results in the formation of needle-shaped crystals 1 – 3 μm in size, and at 100°C/min the size is 4 – 5 μm.

The considered composites based on silicon-organic binders can be used as non-fired coatings, for example, to protect construction materials from gas corrosion at high temperatures. This makes it possible to significantly extend the service life of titanium alloys, steel 09G2S, and alloy 18KhN78T. Thus, when tested in air medium (1200°C), the longevity of titanium alloys increases 14 – 18 times, that of steel 09G2S (1000°C) increases 5 – 7 times, and that of alloy 18KhN78T (1050°C) is 12 – 15 times higher. This increase in the service life of the specified materials at high temperatures is due to the insulating effect of the protective coating consisting of high-strength and heat-resistant sillimanite-mullite phase and corundum firmly adhered to the substrate. The adhesive strength of the coatings to the considered materials at a temperature of 100 – 1100°C is 1.5 – 2.2 MPa.

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